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Catalytic Activity of Ag-Co-MCM-41 for Liquid-Phase Selective Oxidation of Styrene to Benzaldehyde

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A series of Ag-Co-MCM-41 with different metal loadings have been synthesized through the hydrothermal method. All the prepared catalysts were characterized by N_2 adsorption–desorption, X-ray diffraction analysis, transmission electron microscopy. The results revealed that the structure of MCM-41 was well preserved and Ag and Co have been introduced successfully into the mesoporous channels of MCM-41. The liquid-phase catalytic oxidation of styrene on these catalysts was investigated using H_2O_2 as an oxidizing agent and acetone as a solvent in thermostatic water bath. The influence of metal loading, the catalyst dose, temperature, time and styrene/oxidant molar ratio on the conversion of styrene and yield and selectivity of benzaldehyde was investigated. Also, the reusability of the catalysts was evaluated.

Keywords: MCM-41 Mesoporous Material, Ag-Co-MCM-41, Styrene, Oxidation, Benzaldehyde.

1. INTRODUCTION

Oxidation of styrene is a reaction of great interest because its products, mainly benzaldehyde and styrene epoxide, act as versatile and useful intermediates [1–4]. Certainly, benzaldehyde is widely used for the perfumery, pharmaceutical intermediates, dyestuffs and agrochemicals [5]. Therefore, a variety of methods for preparing benzaldehyde have been reported [1, 2, 6–9]. Traditionally, it is produced by hydrolysis of benzal chloride and liquid phase oxidation of toluene [10]. These processes will make the product with chlorine and cause harm to the environment. Recently, much attention has focused on developing eco-friendly aerobic catalytic processes based on efficient catalysts with easy recoverability [11]. The liquid phase selective oxidation of styrene for providing chlorine-free benzaldehyde was developed which H_2O_2 as oxidant. H_2O_2 has many advantages as an oxidant because water is only by-product [12].

However, synthesizing an efficient catalyst is the key to the success of the reaction [13]. Various catalysts, such as metal oxides [14, 15], metals [16], metal doped zeolites, solid acids [17], and metal Schiff bases or Salen complexes [18, 19], have been discussed. Since these homogenous catalysts are usually difficult to separate from the reaction mixture [13], much attention has been focused on immobilizing the complexes on solid supports such as ordered mesoporous silicates [20–25], polymers [26–29], zeolite [30–32] and nanoparticles [33] to afford heterogeneous catalysts. For example, Clara et al. [34] prepared a series of different metal cations incorporated ZSM-5 for the oxidation of styrene to benzaldehyde with H_2O_2 as oxidant. They found that Cr-ZSM-5 exhibited the good catalytic activity, but the conversion of styrene and selectivity for benzaldehyde were only 48.9% and 60.9%, respectively. Islam et al. [28] reported a reusable polymer-anchored Cu(II) complex as the catalyst for this reaction. The conversion of styrene reached 53%, however, the selectivity for benzaldehyde was 52%, and excessive by-product caused the product difficult to recover. In summary, the result was inferior catalytic activity and recoverability [28].

In current work, we prepared a series of Ag-Co-MCM-41 mesoporous materials with different Ag and Co contents. The binding ability of oxygen and Ag is weak, it is easy to break out, and the reduced Ag is relatively difficult to oxidize. Co, on the contrary, binds strongly to oxygen and is not easy to detach, but easy to oxidize. Therefore, the co-introduction of silver and cobalt into MCM-41 mesoporous molecular sieves can assist the catalysis together. The resulting materials were employed

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as catalysts on the styrene selective oxidation using hydrogen peroxide as oxidant under mild reaction conditions, obtaining benzaldehyde as the main product. Key reaction conditions such as metal loading, the catalyst dose, temperature and time and styrene/oxidant molar ratio were investigated. The reusability of the catalysts was also evaluated.

2. EXPERIMENTAL DETAILS

2.1. Chemicals

Styrene (CR), cetyl trimethyl ammonium bromide (CTAB, AR), concentrated sulfuric acid and sodium silicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrogen peroxide (30%H_2O_2, AR) was purchased from Nanjing Chemical Reagent Co., Ltd. Acetone (AR), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$ AR) was purchased from Shanghai Chemical Reagent Co., Ltd. Silver nitrate ($AgNO_3$ AR) was purchased from China Pharmaceutical (Group) Shanghai Chemical Reagent Company.

2.2. Catalyst Preparation

The pure siliceous MCM-41 was synthesized using $Na_2SiO_3 \cdot 9H_2O$ as silicon source and CTAB as template by hydrothermal method, according to the procedure in the literatures [35, 36]. The typical synthetic process was $n(SiO_2):n(CTAB):n(H_2O) = 1:0.2:70$. First, 7.29 g of CTAB was dissolved in 40 ml distilled water until a gelatinous solution was obtained, named solution A. 28.42 g of $Na_2SiO_3 \cdot 9H_2O$ was dispersed into 40 ml distilled water to form solution B. The B solution was poured into a three-necked flask at 35 °C, stirring constantly until completely dissolved, then added the A solution into the flask and continued to stir 30 min. After that, the reaction solution was adjusted to pH = 11 by dropwise addition of sulfuric acid (50 vol.%), and the reaction solution was continuously stirred for another 3 h. Finally, the mixed solution was poured into the autoclave and crystallized at 120 °C for 24 h in an oven. After cooling to room temperature, the sample was filtered, washed with deionized water to neutral, and dried at 60 °C overnight. At last, the samples were heated to 550 °C at a heating rate of 2 °C/min and kept at 550 °C for 6 h, the calcined sample was designated as MCM-41.

The Ag-Co-MCM-41 was directly synthesized by hydrothermal method. A given amount of $Co(NO_3)_2 \cdot 6H_2O$ and $AgNO_3$ (the molar ratio of M/Si = 0.005, 0.01, 0.015 and 0.02) were dispersed in B. Other steps are the same as above. For comparison, the 0.01-Ag-MCM-41 and 0.01-Co-MCM-41 catalysts were prepared in the same manner. Then the samples were pressed tablets at 10 mpa. After grinded, we screened 40–60 mesh particles as catalysts.

2.3. Catalyst Characterization

XRD patterns were recorded on a powder XRD instrument (Rigaku D/max 2500PC) with Cu K_α radiation ($\lambda = 0.15418$ nm) operating at 40 kV and 50 mA in the 2θ range from 1 to 10°. N_2 adsorption–desorption isotherms at 77 K were recorded with a NOVA2000e analytical system made by Quantachrome Corporation (USA). Before measuring, all samples were outgassed at 300 °C for 30 min. Calculation of specific surface area use BET method, while pore size distribution and pore volume were calculated using BJH method. Transmission electron microscopy (TEM) morphologies of samples were observed on a Philips TEMCNAI-12 with an acceleration voltage of 100–120 kV. The Ag and Co content in sample was determined by inductive coupled plasma (ICP) technique (Vista-MPX, Australia), and the detector is MPX CCD. The results are listed in Table I.

2.4. Catalyst Test

The oxidation reaction was performed in a 250 ml round bottom flask with reflux device where vigorous stirring in a thermostat water bath for several hours, the amount of catalyst is 3 wt% of the reactants. Typically, according to a certain proportion, styrene and hydrogen peroxide as raw materials, acetone as solvent, were added to the flask. In the oxidation reaction of styrene, we chose acetone as solvent owing to acetone is relatively stable. If there are no special circumstances, acetone does not normally react with hydrogen peroxide. After the reactions, we chose the catalyst with the best catalytic activity for reusability test. The catalyst was collect, washed with ethanol for 3 times, dried at 60 °C overnight, and then reused [37]. Excess hydrogen peroxide is quenched by sodium thiosulfate during the reaction.

The products were analyzed by gas chromatograph (SP-2000) fitted with a SE-54 capillary column coupled with FID and calculated using normalization method. The column temperature is 120 °C, the detector temperature is 250 °C and the injector is 200 °C.

In the oxidation of styrene, the conversion of styrene, the yield and selectivity of benzaldehyde were calculated by the following formula: $C_{\text{styrene}} = [n_{(\text{styrene, initial})} - n_{(\text{styrene, balance})}]/n_{(\text{styrene, initial})}$ (1); $Y_{\text{benzaldehyde}} = [n_{(\text{styrene, initial})} - n_{(\text{styrene, balance})}]/n_{(\text{styrene, initial})}$ (2); $S_{\text{benzaldehyde}} = n_{\text{benzaldehyde}}/[n_{(\text{styrene, initial})} - n_{(\text{styrene, balance})}]$ (3), where n is the quantity of matter, and C_{styrene}, $Y_{\text{benzaldehyde}}$ and $S_{\text{benzaldehyde}}$ stand for the conversion

Table I. The Ag and Co element content in sample.

Sample	Co-Ag-MCM-41-0.005	Co-Ag-MCM-41-0.001	Co-Ag-MCM-41-0.015	Co-Ag-MCM-41-0.02
W(Ag)%	0.41	0.79	1.02	1.48
W(Co)%	0.22	0.42	0.64	0.85

of styrene, the yield and selectivity of benzaldehyde, respectively.

3. RESULTS AND DISCUSSION

3.1. Catalytic Properties of Ag-Co-MCM-41

3.1.1. XRD Analysis

The low-angle patterns of MCM-41 and *n*-Ag-Co-MCM-41 are depicted in Figure 1(a). The pattern of MCM-41 shows an intense diffraction peak at $2\theta = 2.3°$, which is MCM-41 mesoporous molecular sieve crystal plane peak (100). At the same time, we can see two clearly identifiable (110), (200) diffraction peaks at $2\theta = 3–5°$ are attributed to its characteristic hexagonal pore structure [38]. As compared with the pure silicon MCM-41, the intensity of the (100) diffraction peak of the Ag-Co-MCM-41 sample slightly weakened when the doped metal content is less than or equal to 0.01. When the doped content of metal in Ag-Co-MCM-41 sample is between 0.01 and 0.02, the intensity of diffraction peak decreased obviously, and the diffraction peak became wider and weaker, suggesting that the metal (Ag and Co) doped into the framework of MCM-41 molecular sieve [39]. On the other hand, we found that diffraction peaks shifted to low angle, showing that increasing the spacing of molecular sieves. The reason is ionic radius of the metal ($r_{\mathrm{Co+2}} = 0.065$ nm; $r_{\mathrm{Ag+1}} = 0.115$ nm) is larger than silicon ($r_{\mathrm{Si+4}} = 0.04$ nm). The other one is probably due to the metal ion replaced Si in framework of the molecular sieve. Further, the characteristic diffraction peak weakened with increasing of metal content. This indicated that the ordering of mesoporous molecular sieves gradually declined, and hexagonal structure disappeared. Perhaps metal ions may lead to channel blocking and tunnel collapse. Moreover, the 0.01-Ag-Co-MCM-41 catalyst used reusability test was collected (named as 0.01-Ag-Co-MCM-41 after five runs) and the XRD pattern was shown in Figure 1(a). It is noted that the intensities of the characteristic peaks slightly weakened and the position was almost unchanged. Figure 1(b) shows the wide-angle XRD patterns of the sample. It can be seen that a strong peak is the diffraction peak of silica at about $2\theta = 24.8°$, and several diffraction peaks representing metal oxides appeared between $2\theta = 30$ and $60°$. With the increase of metal loading, the intensity of diffraction peak will be stronger and the diffraction peak of silica will be weaker, which further shows that the metal ions doped on the mesoporous molecular sieve MCM-41.

3.1.2. N_2 Adsorption–Desorption Analysis

The N_2 adsorption–desorption isotherms of the synthesized samples are shown in Figure 2. According to IUPAC classification, the prepared samples are IV type isotherm from the Figure 2. All isotherms exhibit a sharp step at a relative pressure of ca. 0.2–0.4, further showing that all the samples have typical mesostructure with uniform pore size distribution and large pore volumes [40]. The hysteresis loops of the low pressure stage became smaller with the metal loaded increasing. It indicates that the ordering of these materials deteriorated. It also proves the partial pore collapse and obstruction and the samples regularity decreased.

From Table II, the specific surface areas and pore volumes of all the samples synthesized decrease with the increase of the amount of metal added. Combined with the results of XRD and N_2 adsorption–desorption isotherms, it is reasonable to conclude that the ordering of the synthesized mesoporous molecular sieves decreases with the increase of the amount of metal added.

3.1.3. Transmission Electron Microscopy Analysis

Figure 3 shows TEM images of the prepared samples. As shown in Figure 3, all the four samples exhibit a hexagonal mesoporous structure of MCM-41. Showing that these samples have mesoporous structure and Ag-Co-MCM-41 mesoporous molecular sieves were successfully synthesized. Materials still retains mesostructure when the loaded metal content is less than or equal to 0.01, but the mesoporous ordering decreases. While the metal content continues to increase, the pore structure disappeared. We can conclude that metal loaded changed the order of the samples.

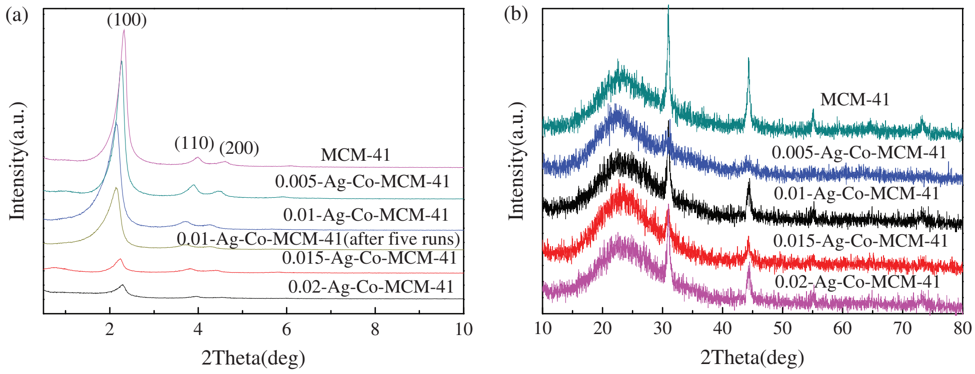

Figure 1. XRD patterns of Ag-Co-MCM-41 samples with different M/Si molar ratios: (a) the low-angle patterns; (b) the wide-angle patterns.

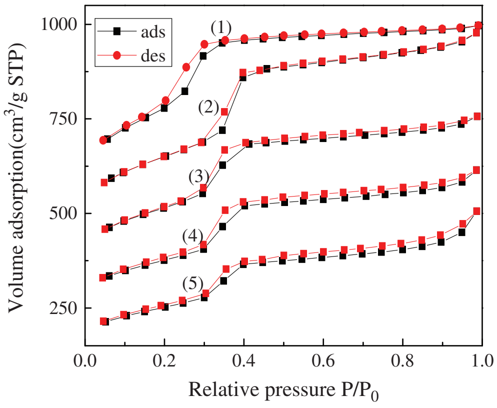

Figure 2. N_2 adsorption–desorption isotherms of samples. (1) MCM-41; (2) 0.005-Ag-Co-MCM-4; (3) 0.01-Ag-Co-MCM-41; (4) 0.015-Ag-Co-MCM-41; (5) 0.02-Ag-Co-MCM-41.

3.2. Optimization of Reaction Conditions

The results of styrene oxidation over Ag-Co-MCM-41 in acetone solution are carried out as following experiment. The main product of the reaction is benzaldehyde, possibly, the others could be found, such as styrene oxide, phenylacetaldehyde, benzoic acid and so on.

3.2.1. Effect of Ag and Co Loaded

0.1 moL styrene was added to 250 mL flask, the amount of catalyst was 3% of the mass fraction of styrene, oxidant and solvent were added according to the mole ratio of styrene:hydrogen peroxide:acetone = 1:3:2, in which hydrogen peroxide was used as oxidant and acetone as solvent. The reaction temperature was 60 °C and the reaction time was 7 h. The catalytic reaction takes place in a water bath pot with constant temperature and constant speed stirring. The catalyst was *n*-Ag-Co-MCM-41 (n = 0.005, 0.01, 0.015, 0.02). The results are as shown in Figure 4. It can be seen that the conversion of styrene gradually increased with the increasing of metal loading amount, suggesting that the catalytic activity of Ag-Co-MCM-41 catalyst enhanced with the increasing of metal loading amount. This may be due to an increase in the amount of active sites in samples. On the other hand, we found that selectivity of benzaldehyde gradually decreased with the increasing of metal loading amount. This is probably due to the increase of metal loading enhances the catalytic activity of catalyst, therefore, the oxidation process eased and resulted in higher amounts of by-products.

Table II. Surface areas and pore sizes of MCM-41 and Ag-Co-MCM-41 samples with different M/Si molar ratios.

Samples	Surface area/ (m^2/g)	Average pore size/ (nm)	Total pore volume/ (cm^3/g)
MCM-41	1102.80	3.46	0.97
0.005-Ag-Co-MCM-41	908.30	3.56	0.89
0.01-Ag-Co-MCM-41	794.17	3.93	0.71
0.015-Ag-Co-MCM-41	642.92	3.99	0.64
0.02-Ag-Co-MCM-41	551.75	4.55	0.63

3.2.2. Effect of Catalyst Dose

0.01-Ag-Co-MCM-41 molecular sieve was used as catalyst for the reaction. The amounts of catalyst were 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, respectively. Other reaction conditions remain unchanged. The result of the reaction is shown in Figure 5. It can be seen that with the increasing amount of catalyst, there is a maximum conversion of styrene, because when the catalyst content is low, increasing the amount of catalyst can increase the amount of hydrogen peroxide adsorbed by the catalyst, resulting in the formation of many more active, therefore, the conversion of styrene increased [41]. When the amount of catalyst exceeded a certain amount, the conversion of styrene decreased. This is due to the increase in the amount of catalyst used to aggravate the decomposition of part of hydrogen peroxide, resulting in a decrease in the conversion of styrene. Further, when the catalyst weight was 3 wt%, the conversion of styrene and the yield of the benzaldehyde were 45.2% and 24.1% respectively, and the selectivity of benzaldehyde was 53.3%.

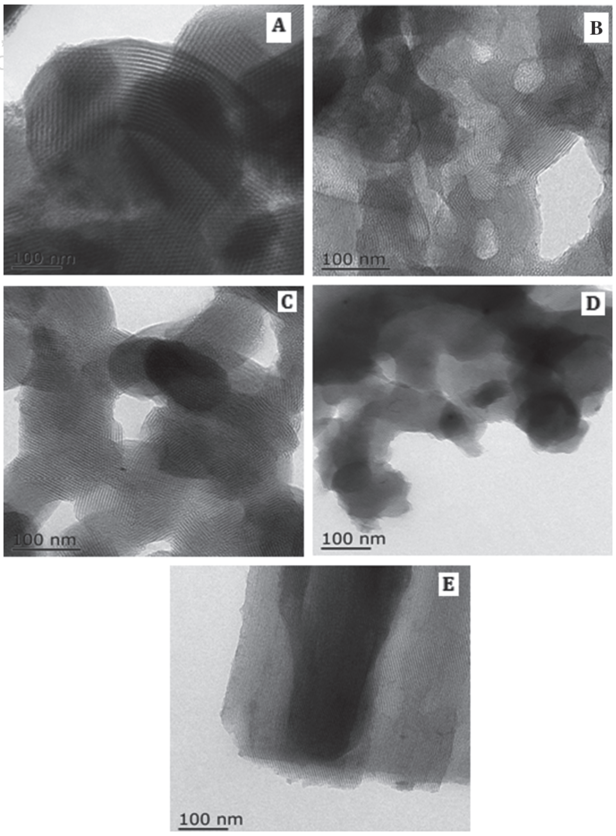

Figure 3. TEM images of various samples: (A) MCM-41; (B) 0.005-Ag-Co-MCM-41; (C) 0.01-Ag-Co-MCM-41; (D) 0.015-Ag-Co-MCM-41; (E) 0.02-Ag-Co-MCM-41.

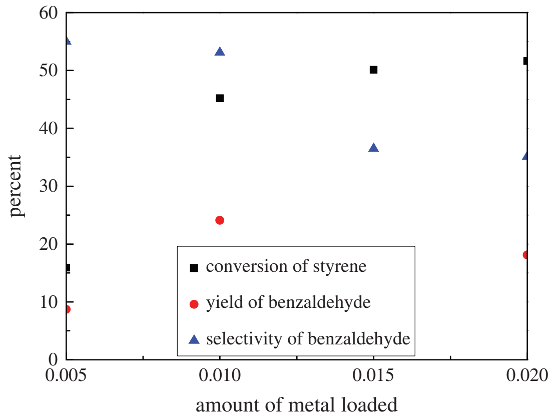

Figure 4. Effect of amount of metal loaded (reaction condition: Catalyst dose = 3 wt% of the reactants; temperature = 60 °C; time = 7 h; $n_{\text{styrene}}/n_{\text{H}_2\text{O}_2} = 1{:}3$).

3.2.3. Effect of Reaction Time

According to the above experiments, 0.01-Ag-Co-MCM-41 was selected as the catalyst, the reaction time was 5, 6, 7, 8 and 9 h respectively, and the other conditions were unchanged. The results are shown in Figure 6. As shown in Figure 6, when the reaction time increased from 5 to 6 h, the conversion of styrene and the yield of benzaldehyde are slightly increased. When the reaction time is 7 h, the conversion of styrene and the yield of benzaldehyde increased rapidly. This may be because the reaction time is relatively short, only part of the reactant reaction. When the reaction time continued to increase, the conversion of styrene was almost unchanged, while the yield of benzaldehyde began to decrease, because with the reaction time prolonged, the product continued to take place deep oxidation, resulting in a decrease in selectivity. This suggested that the longer time is not more conducive to the occurrence of the reaction. Therefore, 7 h was chosen as the reaction time for the follow-up reaction.

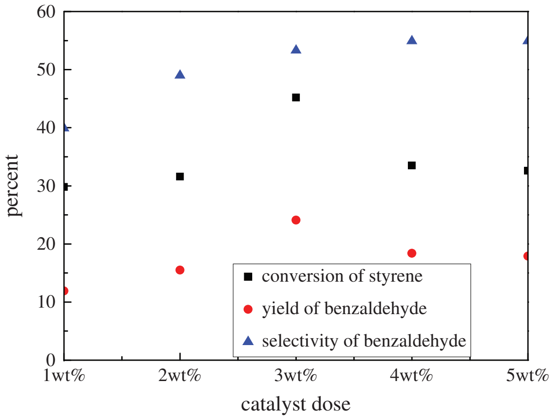

Figure 5. Effect of catalyst dose (reaction condition: Time = 7 h; temperature = 60 °C; the loaded amount of the metal = 0.01; $n_{\text{styrene}}/n_{\text{H}_2\text{O}_2} = 1{:}3$).

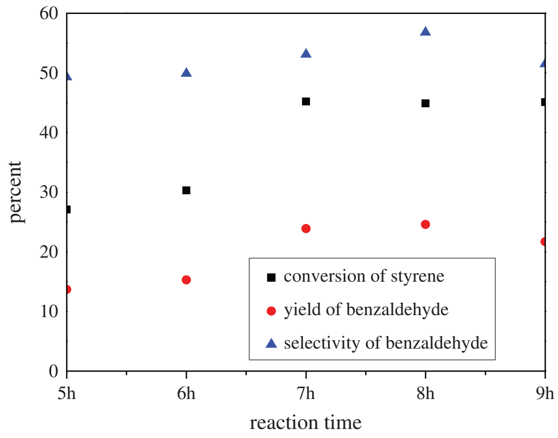

Figure 6. Effect of reaction time (reaction condition: Catalyst dose = 3 wt% of the reactants; temperature = 60 °C; the loaded amount of the metal = 0.01; $n_{\text{styrene}}/n_{\text{H}_2\text{O}_2} = 1{:}3$).

3.2.4. Effect of Reaction Temperature

According to the above experiments, 0.01-Ag-Co-MCM-41 was selected as the catalyst, the amount of catalyst was 3 wt%, the reaction time was 7 h, and the reaction temperature was 50, 60, 70, 80 and 90 °C, respectively. The other experimental conditions were not changed. The experimental results are showed in Figure 7. We found from Figure 7 that with the increase of reaction temperature, the conversion of styrene, the yield and selectivity of benzaldehyde increased first and then decreased. The maximum conversion of styrene was 65.2% at 80 °C, the maximum yield of benzaldehyde was 28.9% at 70 °C, and the maximum selectivity of benzaldehyde was 53.5% at 60 °C. However, when the reaction temperature reaches 90 °C, the conversion of styrene increased. This may be attributed to the decomposition of some oxidants and the partial volatilization of acetone caused by the high reaction temperature. The reduction of acetone content is not conducive

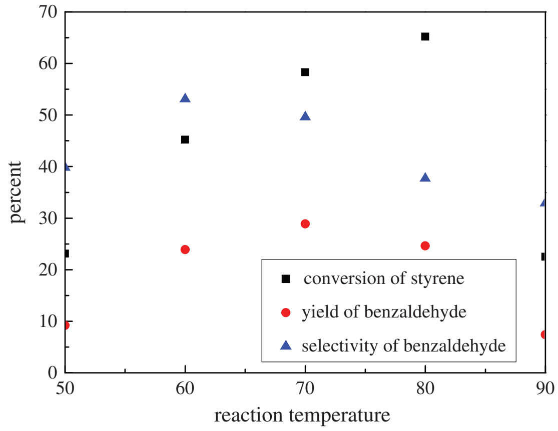

Figure 7. Effect of reaction temperature (reaction condition: Catalyst dose = 3 wt% of the reactants; time = 7 h; the loaded amount of the metal = 0.01; $n_{\text{styrene}}/n_{\text{H}_2\text{O}_2} = 1{:}3$).

to the mass transfer between styrene and hydrogen peroxide, which makes styrene and hydrogen peroxide not easily adsorbed on the active site on the surface of the catalyst, so that the conversion of styrene decreases.

3.2.5. Effect of Molar Ratio of H_2O_2 to Styrene

Figure 8 shows the effect of different molar ratios of styrene to H_2O_2 on the oxidation of styrene onto 0.01-Ag-Co-MCM-41 catalyst with the reaction temperature of 60 °C and the reaction time of 7 h, the molar ration of styrene to H_2O_2 was 1:2, 1:2.5, 1:3, 1:3.5 and 1:4, respectively. The results showed that the conversion of styrene increased with the increase of the ratio of hydrogen peroxide, and the smooth trend was observed when the ratio is over 1:3. This may be due to when the amount of hydrogen peroxide increases, the amount of H_2O_2 adsorbed in the pores of catalyst also increases. There are sufficient active oxygen sources in the oxidation process of styrene, thus improving the conversion of styrene. In addition, when the amount of hydrogen peroxide is lower than the chemical reaction metering ratio, the hydrogen peroxide content is less, the concentration is lower, and the effect of increasing the conversion of styrene is not very obvious. When the amount of hydrogen peroxide is close to the chemical reaction metering ratio, the conversion of styrene increased obviously. When the amount of hydrogen peroxide continued to increase, due to the dilution of water in 30% hydrogen peroxide, the increase of oxidant concentration in the reaction system was not obvious, so that the conversion of styrene tended to change smoothly. Further, it is noted from Figure 8 that when the molar ratio of styrene to H_2O_2 was 1:3, the benzaldehyde selectivity and benzaldehyde yield reached the maximum, respectively. Continue to increase the styrene/H_2O_2 molar ratio, and the reaction concentration would be diluted, resulting in the decrease in catalytic activity and benzaldehyde yield. In this case, more styrene oxide as the main byproduct was produced, leading to the decrease of the selectivity of benzaldehyde.

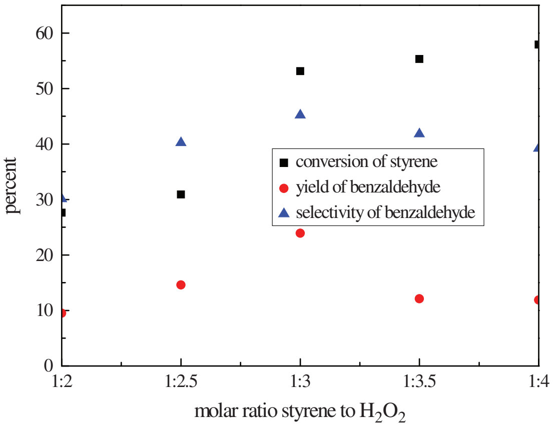

Figure 8. Effect of molar ratio of styrene to H_2O_2 (reaction condition: Catalyst dose = 3 wt% of the reactants; temperature = 60 °C; the loaded amount of the metal = 0.01; time = 7 h).

Table III. Results of the catalytic oxidation of styrene over different catalysts.

Sample	Conversion of styrene (%)	Selectivity of benzaldehyde (%)	Yield of benzaldehyde (%)
0.01-Co-MCM-41	35.6	43.8	15.6
0.01-Ag-MCM-41	28.9	37.7	10.9
0.01-Ag-Co-MCM-41	45.2	53.3	24.1

Notes: Reaction condition: Catalyst dose = 3 wt% of the reactants; temperature = 60 °C; the loaded amount of the metal = 0.01; time = 7 h, $n_{\text{styrene}}/n_{H_2O_2} = 1:3$.

3.2.6. Effect of Different Catalysts

Table III listed the catalytic results obtained onto different catalysts. According to the Table III, the 0.01-Ag-Co-MCM-41 catalyst exhibits high catalytic activity as compared with the 0.01-Co-MCM-41 and 0.01-Ag-MCM-41 catalysts. This is probably attributed to the co-introduction of silver and cobalt into MCM-41 mesoporous molecular sieves could assist the catalysis together.

3.2.7. Catalyst Reusability

In the experiment of catalytic oxidation of styrene to benzaldehyde, the stability of the catalyst was studied. Under the optimum reaction conditions, the catalyst used in the first time was recovered, and then the impurities were removed by washing anhydrous ethanol for many times. Put in the oven dry, the resulting samples continue to use, repeat five times and observe the catalytic effect. The results summarized in Figure 9 show that the 0.01-Ag-Co-MCM-41 could be successfully used five times without significant loss of the activity. The slight decrease in selectivity for recovered catalyst is probably due to residual organics on catalyst impeding desorption of benzaldehyde from the catalytic centers, leading to over oxidation to benzoic acid.

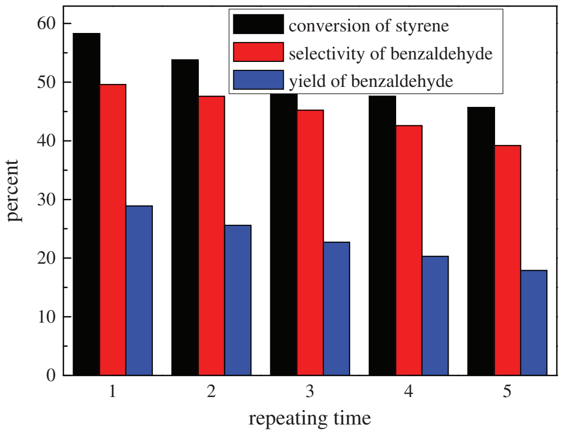

Figure 9. Catalyst reusability.

4. CONCLUSIONS

In this paper, different proportions of Ag-Co-MCM-41 were prepared by direct synthesis. The catalytic oxidation of styrene on Ag-Co-MCM-41 catalyst was studied in details. The optimum reaction conditions are as follows: catalyst dose is 3 wt% of the reactants, temperature is 60 °C, time = 7 h, $n_{\text{styrene}}/n_{H_2O_2}$ is 1:3, and the loaded amount of the metal is 0.01. As compared with the Ag-MCM-41 and Co-MCM-41, the catalytic activity of Ag-Co-MCM-41 catalyst in oxidation of styrene enhanced. The Ag-Co-MCM-41 catalyst could be used five times without significant loss, suggesting that the Ag-Co-MCM-41 catalyst had good stability. Also, the Ag-Co-MCM-41 catalyst is a promising catalyst for the catalytic oxidation reaction of styrene.

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